### PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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#### **Abstract**

A significant component of the U.S. DOE Hydrogen Program is the development of a practical technology for the direct production of hydrogen using a renewable source of energy. High efficiency photoelectrochemical systems to produce hydrogen directly from water using sunlight as the energy source represent one of the technologies identified by DOE to meet this mission. Reactor modeling and experiments conducted at UH provide strong evidence that direct solar-tohydrogen conversion efficiency greater than 10% can be expected using planar photoelectrodes fabricated from low-cost, multijunction (MJ) amorphous silicon solar cells. Solar-to-hydrogen conversion efficiencies as high as 7.8% have been achieved using a 10.3% efficient MJ amorphous silicon solar cell, and higher efficiency can be expected with continued cell and reactor optimization. Further, conversion efficiencies exceeding 15% may be possible using side-byside series-connected copper indium diselenide cells in a fully integrated and encapsulated photoelectrode design developed this year. Critical photoelectrode materials issues necessary to long-term sustained photoelectrolysis have been addressed under this project, including development of: hydrogen and oxygen catalyst films exhibiting no measurable degradation in 1N KOH after 3 years of operation; ITO top contact films optimized for transparency, conductivity and KOH resistance; device-grade amorphous silicon films resistive to KOH; and TiO<sub>2</sub> encapsulation films optimized for transparency and stability in KOH.

#### Introduction

One of most ambitious goals of the US Department of Energy's Hydrogen Program is the large-scale production of hydrogen utilizing a renewable energy source to split water. High efficiency photoelectrochemical systems to produce hydrogen directly from water using sunlight as the energy source is one of the technologies identified by DOE to meet this mission. In order to meet DOE goals, such a system must be low cost, must operate at solar-to-chemical conversion efficiencies greater than 10% and must have long operating lifetimes. Although numerous approaches involving a variety of semiconductors have been explored since the early 1980's, progress has been slow, limited by the high voltage required to dissociate water and corrosiveness of the aqueous electrolytes. Modeling and proof-of-concept experiments conducted at UH provide strong evidence that future direct solar-to-hydrogen conversion efficiency greater than 10% can be expected with photoelectrodes fabricated from low-cost, multijunction (MJ) amorphous silicon solar cells. Based on the very thin semiconductor layers involved and on compatibility with high-throughput manufacturing processes, these systems have the potential for very low cost.

In the past, our effort was mostly focused on demonstrating the feasibility of the photoelectrochemical approach, and on improving photoelectrode efficiency by optimizing the hydrogen and oxygen catalysts. To date, solar-to-hydrogen efficiencies as high as 7.8% have been achieved using a 10.3% efficient MJ solar cell (Rocheleau et al., 1998). Higher efficiency can be expected with the use of higher efficiency solar cells: 13% is the current world record efficiency for stabilized amorphous silicon (Yang, et al.,1997). Additional improvement in solar-to-hydrogen efficiency is expected from further reduction in the anodic and cathodic overpotentials, optimization of the solar cell for hydrogen production rather than electricity production, and the use of advanced materials (such as CIS) in a side-by-side series-connected mode using a new integrated photoelectrode design developed this year.

After successful demonstration of proof of concept, we have focussed this year on the critical engineering issues for practical implementation. The main goal was the development of a fully-integrated photoelectrode configuration (based on planar fabrication of thin films onto inexpensive substrates) which is stable in aqueous electrolyte, and which is amenable to scale-up. The current research has focused on 1) photoelectrode design; 2) optimization of the electronic and corrosion-resistance properties of the underlying semiconductor structures and of the transparent conductive top contact; and 3) development of a highly transparent protective coating impervious to electrolyte corrosion. Since the efficient thin film catalysts developed in previous years have demonstrated long-term corrosion resistance in KOH, this electrolyte has been selected as the basis for our photoelectrolysis reactors. To date there has been significant progress in enhancing the KOH-resistance of both i- and p-layer amorphous silicon, and of transparent/conductive ITO. Additionally, highly transparent films of TiO<sub>2</sub> for photoelectrode encasement have been demonstrated with excellent stability in KOH.

In this report we describe progress in several parallel efforts including photoelectrode design and fabrication, optimization of the various photoelectrode thin film materials,

construction of a test reactor for photoelectrode testing, and ongoing work on photoelectrode/reactor modeling for advanced designs.

# Scope/Technical Approach

For the past several years, our approach has been to compare alternate materials and system configurations using reactor modeling, and to identify and address the critical materials and photoelectrode-operation issues through extensive experiments in materials synthesis and in photoelectrode fabrication and testing. Last year, we shifted our focus from the glass superstrate cells produced by Solarex to metal substrate cells (e.g., those produced by Energy Conversion Devices) for compatibility with proposed conceptual designs. These reactor designs, prepared in collaboration with NREL, indicated several important advantages of using the solar cell configurations traditionally fabricated onto metal substrates. This year, we completed the design of a fully-integrated and self-contained photoelectrode fabricated entirely with thin film processing onto metal substrates. We've made significant advances in optimizing the electronic properties and corrosion resistance of the semiconductor, transparent-conductor and transparent-protective films for the new photoelectrode. We have also continued our strategy of working closely with the solar cell manufacturers to obtain high-efficiency solar cell device structures tailored specifically for hydrogen production. We are currently working on developing the specific processing steps for fabrication of the integrated photoelectrode and on a mid-scale photoreactor for testing the hydrogen production capacity of several photoelectrodes operated in parallel.

#### Results

# Loss Analysis

In 1991 we began a systematic analysis of semiconductor materials and photoelectrode designs (Rocheleau and Miller, 1997; Rocheleau et al., 1997; Rocheleau and Vierthaler, 1994) to compare the potential hydrogen production rates of different semiconductor materials and in various single and multijunction configurations. This study showed that series-connected multijunction (MJ) devices could be designed to operate at voltages optimized for direct water splitting while still using a large fraction of the available solar spectrum resulting in significantly higher efficiencies than conventional single junction (single photon) systems. The multijunction approach also eliminates the need for direct contact between the semiconductor and electrolyte allowing the use of protective films to prevent corrosion. Of the photovoltaic technologies which are sufficiently developed to be considered for hydrogen production (namely, Group III-V crystalline cells and amorphous silicon) the high quality III-V materials were clearly shown to have the potential for higher solar-to-hydrogen conversion efficiencies. However, their high-cost makes them impractical for commercial PEC systems.

Surprisingly, the solar-to hydrogen conversion efficiencies predicted for the much lower cost multijunction amorphous silicon ranged up to 50% of those calculated for the best Group III-V heterojunctions. Based on the scale of manufacture under development for amorphous silicon, and on the related cost reductions predicted by the PV industry for a-Si thin-film technologies, the UH program has focused to date on MJ amorphous silicon devices in the development of high efficiency photoelectrodes. Interestingly, the advanced photelectrode design developed this year also allows for multijunction devices seriesconnected in a planar configuration in addition to monolithic stacked. This has opened the door to higher solar-to-hydrogen efficiencies using a new class of low cost semiconductor materials, e.g., thermally evaporated copper indium diselenide (CIS).

This year we initiated an effort to upgrade the loss analysis model. Planned improvements include the incorporation of a sophisticated commercially-available optics modeling software package, and expansion of the integrated electrical/optical model to cover additional photoelectrode materials and configurations, such as the parallel-connected CIS cells.

## Photoelectrode Design

Largely as a result of directions indicated by the loss analysis effort, the photoelectrode design for direct splitting of water into hydrogen and oxygen has evolved through several stages since the inception of the Hydrogen Program at UH. This evolution is traced in Figure 1. As shown in Figure 1a, the original configuration used single-crystal p-type silicon with an OER catalyst layer on the back surface, and scattered islets of platinum HER catalyst deposited onto the front, light-entering surface. Here the semiconductor/electrolyte junction forms the photovoltaic diode, and the HER islets facilitate current exchange. In the second stage photoelectrode, shown in Figure 1b, the front surface is evenly coated with Shottky-barrier metal followed by HER catalyst layers thin enough for optical transmission, effectively replacing the semiconductor/liquid junction with a rectifying semiconductor/metal junction. The first two designs were fabricate using planar processing exclusively and were fully integrated on a single substrate. While these did result in a net energy savings, the voltage generated was below that required to split water, necessitating external biasing. Corrosion resistance was also poor.

The third generation photoelectrode shown in Figure 1c incorporated several breakthrough features: first the single-junction crystalline silicon diode is replaced by a triple-junction amorphous silicon diode (a pinpinpin deposited onto a glass/CTO substrate in this configuration); secondly, the HER and OER thin-film catalysts are, respectively, sputter-deposited CoMo and Fe:NiOx (Miller and Rocheleau, 1997) developed at UH specifically for low overpotentials and for long life in KOH (no performance degradation observed after 3 years of continuous operation.) The small prototype reported in 1997 and 1998 (Rocheleau et al., 1998, Rocheleau et al., 1997) based on this configuration achieved solar-to-hydrogen efficiencies up to 7.8% (using the lower heating value of hydrogen). Also, since only catalyst surfaces are exposed to the electrolyte, excellent corrosion resistance was also achieved. The primary disadvantage here is the use of separated electrodes and the

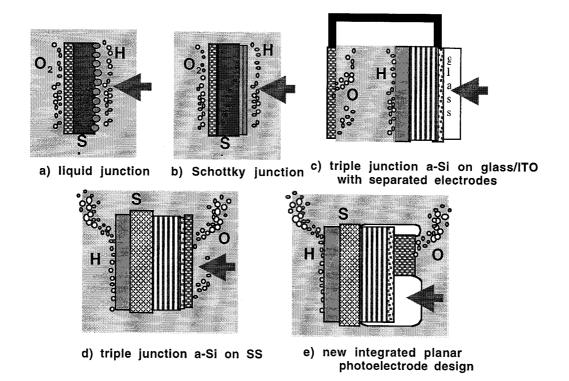


Figure 1: Evolution of the planar photoelectrode for solar-to-hydrogen conversion.

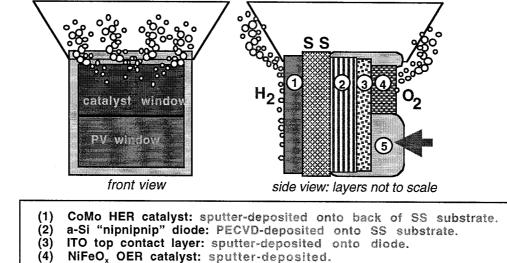


Figure 2: Processing steps for the fully integrated planar photoelectrode.

(5) TiO2 protective window: sputter-deposited.

need for external wiring, features which could prove prohibitive according to preliminary comparative cost-estimates of conceptual photoreactor designs.

The external wiring is eliminated in the photoelectrode shown in Figure 1d. A stainless steel substrate is coated on the front side with a triple nipnipnip junction amorphous silicon diode and thin ITO and OER catalyst films, and on the back side with HER catalyst. The disadvantage is that light must enter through the OER catalyst leading to additional optical loss. With the metal oxide catalyst developed to date, films thin enough for good optical transmission offer little corrosion protection to underlying films, necessitating highly corrosion-resistant ITO and amorphous silicon. These photoelectrodes are fully integrated onto a single substrate and are fabricated using all planar processing techniques, however the prototypes constructed all suffered from reduced efficiency due to the optical losses and from poor stability in KOH due to the thin catalyst layer.

The second major breakthrough came this year in the development of the fifth generation photoelectrode pictured in Figure 1e. A more detailed view of the structure along with a description of the planar processing steps is shown in Figure 2. The important new feature of this design in the incorporation of a highly transparent and corrosion resistant thin film material (such as sputtered TiO<sub>2</sub>) which acts as a protective encapsulation, but does not laterally transport current and therefore does not need to be conductive. As in the previous configuration, HER catalyst (CoMo) is sputter-deposited onto the back of a stainless steel substrate, and a-Si nipnipnip and ITO layers are deposited onto the front. Next, OER catalyst (Fe:NiOx) is sputter-deposited through a shadow mask onto a specified fraction of the diode's surface, and the TiO<sub>2</sub> encapsulation film is sputtered through a second mask onto the remaining fraction. Light enters through the encapsulation fraction while current is transported through the catalyst fraction; this precludes the need for ultra-thin/transparent OER catalyst films. High efficiency will require modest concentration to focus the light onto the transparent region of the surface.

The new photoelectrode design is fully integrated onto a single substrate using a sequence of straightforward planar processing steps. A significant advantage is that only high stability surfaces (i.e., the thick catalyst films and the TiO<sub>2</sub> encapsulation film) are exposed directly to electrolyte. One disadvantage is the added component of lateral current collection. Therefore, optimization of this photoelectrode requires the proper design of OER and encapsulation window geometries to maximize light throughput while minimizing lateral collection losses. The device can also be optimized by tailoring thicknesses of the ITO film for enhanced lateral conductivity and the TiO<sub>2</sub> film for reduced front surface reflection. The loss analysis model is being modified to allow optimization of the planar integrated photoelectrode performance.

Critical for the success of any photoelectrode design is the optimization of materials properties of all the constituent films. For example, although only the catalyst and encapsulation films are exposed to electrolyte in the generation five (1e) integrated photoelectrode, the entire film stack must remain corrosion-free over extended exposure to the harsh KOH environment. Progress in enhancing corrosion resistance and other electronic properties in the constituent materials is detailed in the following section.

## **Materials Optimization**

An important emphasis this year has been to address the critical photoelectrode materials issues necessary for long-term sustained photoelectrolysis. Significant progress has included the development of: 1) hydrogen and oxygen catalyst films exhibiting no measurable degradation in 1N KOH after 3 years of operation; 2) device-grade amorphous silicon films resistive to KOH; 3) ITO top contact films optimized for transparency, conductivity and KOH resistance; and 4) TiO<sub>2</sub> encapsulation films optimized for transparency and stability in KOH.

## Catalysts

Over the past several years, the University of Hawaii has developed stable high performance catalysts for hydrogen-producing planar photoelectrodes. Reactively-sputtered layers of Fe:NiOx with high activity for oxygen evolution have been demonstrated and reported in detail elsewhere (Miller and Rocheleau, 1997; Miller, 1996), and reactively-sputtered films of cobalt/molybdenum with excellent stability and high hydrogen evolution activity have been developed. Since these thin film catalysts are in direct contact with the electrolyte in any photoelectrode configuration, stability under normal operating conditions is essential. Last year we reported that no performance degradation was observed in the Fe:NiOx and CoMo films after 13,600 hours of continuous testing at a current density of 20 mA/cm² in 1N KOH. This year, the stability testing was successfully concluded with no overpotential increases observed after 3 years of continuous operation.

# Amorphous silicon

During this year, considerable effort was expended in upgrading the amorphous silicon deposition system to enhance our ability to make device quality materials, in particular, ptype and n-type amorphous silicon films. The main reaction chamber for the Plasmaenhanced CVD system (PECVD) is shown in Figure 3. Over the past several months, we have made significant progress in the fabrication of high voltage (> 0.8V) single junction "pin" diodes, demonstrating the device quality of the doped layers. Figure 4 demonstrates the recent improvements in the JV behavior (Figure 4a) and the quantum efficiency characteristics (Figure 4b) of our in-house deposited "pin" cells. The high series resistance in these cells is attributable to a very thick i-layer and a thin, highly-resistive p-layer developed for specific tests. Lower resistance devices with higher efficiency are under development. While the in-house single junction cells provide convenient samples for materials and device characterization, it is our intent to obtain triple junction samples from the University of Toledo which has had considerable experience in fabricating high efficiency multijunction amorphous silicon devices. Contract negotiations with the University of Toledo have recently been completed.

A major emphasis this year has been to optimize corrosion resistance of all layers in the photoelectrode structure without compromising device performance. Although we previously reported stability in (1N) KOH for intrinsic amorphous silicon films when carbon was added to widen the bandgap, the addition of boron to produce p-type films

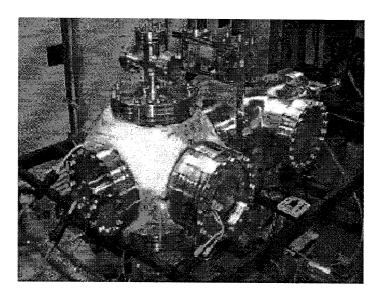


Figure 3: Plasma-enhanced CVD system for amorphous silicon.

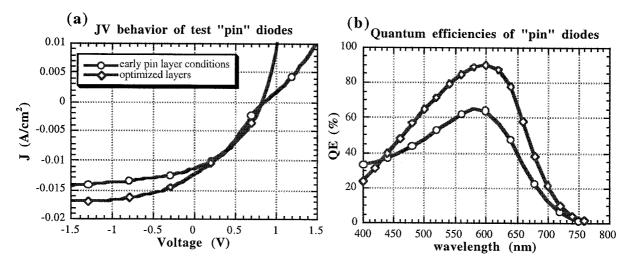


Figure 4: Progress in device quality of fabricated amorphous silicon "pin" diodes.

(the outermost active layer of the n-i-p structure) resulted in high corrosion currents and visual dissolution of the films. While our current planar photoelectrode design does not require a chemically resistant p-layer, corrosion resistance in the amorphous silicon films would enhance the device lifetime in KOH by reducing susceptibility to degradation from surface scratches and pinholes.

During this year, we have developed device-grade silicon-carbide p-layers which do not dissolve in the KOH, even when subjected to large reaction current densities (Hihara et al.,

1999). Specific process changes that yielded these higher-stability films include more moderate hydrogen dilution (approximately 1:1 H<sub>2</sub>: (CH<sub>4</sub>+SiH<sub>4</sub>), lower plasma power and lower gas pressure. Boron-doped p-layers deposited under these conditions incorporated into single junction "pin" test device structures have demonstrated open circuit voltages in excess of 800mV and quantum efficiencies exceeding 90%, as shown in Figure 4, but these devices have not yet been optimized for solar efficiency.

P-layers deposited onto nickel substrates were tested electrochemically in 1N KOH to evaluate their chemical stability. The films were subjected to an initial 'burn-in' by passing a constant current density of 20mA/cm<sup>2</sup> through the films for 10 minutes. After the burnin, a slow cyclic voltammetric scan (lasting approximately 90 minutes) was performed during which current densities as high as 100mA/cm<sup>2</sup> were measured. By visual inspection, the new p-layers showed no signs of dissolving in the KOH despite being subjected to these relatively high current density levels. This is shown in Figure 5, which compares the surfaces of the old and new p-layers after electrochemical testing. A 1cm<sup>2</sup> circular area in the center of each was subjected to the KOH tests, where the old films are seen to dissolve while the new optimized films do not. The voltammetric scan for one of the optimized films is shown in Figure 6. Although there was no visible change in the film's physical appearance, the hysteresis observed between the forward and backward sweeps in the figure is indicative of some surface modification during the chemical current exchange. This effect is being further explored. The important result is that we have successfully deposited boron-doped Si:C layers which function electronically in the "pin" device configuration and which do not dissolve readily in KOH. This represents a significant advance over all previously reported films.

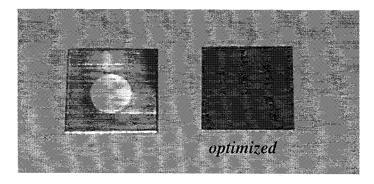


Figure 5: Improvement in p-layer KOH corrosion resistance.

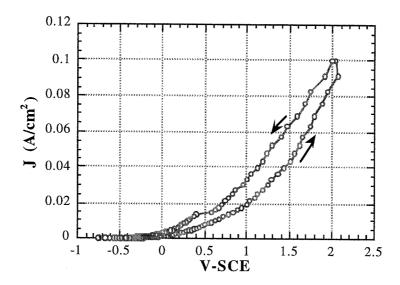


Figure 6: Cyclic voltammetry of improved p-layer films in 1N KOH.

#### ITO

This year we have also concentrated on optimizing the next layer in our multilayer photoelectrode design: indium-tin-oxide (ITO) for use as a transparent conductive front contact. ITO has been has been actively researched for use in solar cells where process conditions are varied to optimize the balance between conductivity and light transmission (Danson et al., 1997). For hydrogen photoelectrolysis, chemical resistance in the electrolyte, in our case, KOH is also critical.

At UH, thin films of ITO have been deposited by RF sputtering from a compound ITO target. A test matrix covering a range of process conditions including: sputter gas composition from 0 to 0.67% oxygen in argon; RF sputter power from 50 to 150W and substrate temperature from 75 to 100°C. For each set of conditions, films were deposited onto glass for conductivity (4-point probe), transparency (photospectrometer) and structural (XRD) measurements; onto silicon for thickness (profilometer) and composition (EDX) measurements; and onto nickel for electrochemical and corrosion experiments in KOH.

Results from the test matrix clearly indicate that the film properties vary significantly over the range of conditions used in the sputtering system. For example, good film transparency requires some oxygen content in the sputtering gas, as illustrated in Figure 7 which compares the optical absorption as a function of wavelength in ITO films deposited with 0% and 0.4% oxygen in argon. However, too much oxygen results in reduced film

conductivity as shown in Figure 8. For example, in all films deposited with 0.67% oxygen, the measured conductivities were below  $333(\Omega\text{-cm})^{-1}$  (reaching as low as 0.02), whereas

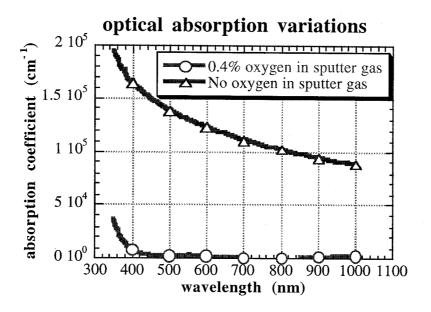


Figure 7: Effect of oxygen in sputter gas on optical absorption in ITO films.

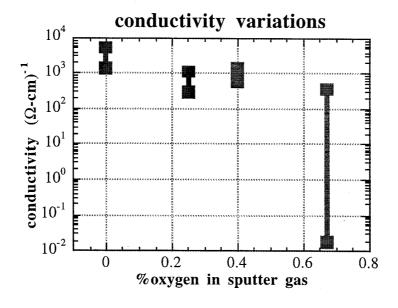


Figure 8: Effect of oxygen in sputter gas on electrical conductivity in ITO films.

conductivity values in films deposited with 0, 0.25 and 0.4% oxygen all ranged between 700 and 1350  $(\Omega\text{-cm})^{-1}$ .

From corrosion experiments performed to date, it is apparent that the degree of chemical stability of the ITO films in KOH also depends strongly on process conditions. Each ITO film deposited onto nickel foil was subjected to an initial 10 minute 'burn-in' period at a constant current density of 20mA/cm<sup>2</sup> followed by a slow cyclic voltammetric scan (lasting approximately 90 minutes). Current densities as high as 100mA/cm<sup>2</sup> were measured at the highest bias conditions. Films deposited at higher substrate temperatures and at higher deposition rates (i.e., higher sputter powers) demonstrate improved chemical resistance in the KOH environment. This is illustrated in Figure 9 which compares the voltammetry curves for ITO films deposited under conditions of 4% oxygen, 50 Watts and 75°C versus conditions of 4% oxygen, 100W and 100°C. The reduced hysteresis observed in the latter indicates reduced surface modification and enhanced stability in KOH, even under conditions where reaction currents are high compared with anticipated operating condition of the photoelectrodes. The superior corrosion resistance in the 100W/100°C film is obvious from a visual inspection of the film surfaces after corrosion testing, as seen in Figure 10, where the optimized film is pictured on the right. Fortunately, this ITO optimized for KOH stability is deposited under conditions yielding high conductivity and transparency, making it a well suited material for the top conductive contact layer in the integrated photoelectrode structure.

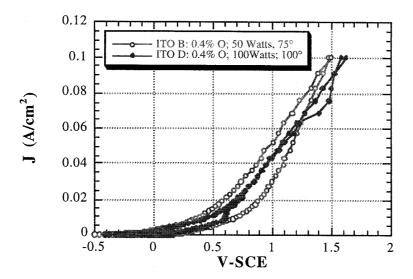


Figure 9: Cyclic voltammetry of different ITO films in 1N KOH.

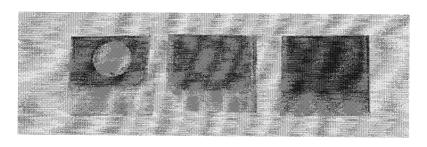


Figure 10: KOH resistance in ITO films deposited under different conditions.

### TiO2

A unique feature of the new integrated photoelectrode is the use of a highly transparent and highly stable encapsulation layer which also serves as an optical window for sunlight. Two candidate materials currently under consideration are TiO2 (rf sputtered from a compound target) and undoped amorphous silicon carbide (rf PECVD) To date more extensive characterization of the TiO2 films has been performed, and these tests have indicated that this material can be deposited to have the appropriate optical and chemical stability properties. Several TiO<sub>2</sub> films were sputter deposited over a range of rf sputtering conditions. The film with the best optical and corrosion resistant characteristics was sputtered in 10mTorr of 0.4% O in Ar at an rf power of 450W. Relevant properties of this optimized film are shown in Figure 11. As seen in Figure 11a, which shows absorption coefficient calculated from photospectrometer measurements of transmittance and reflectance, optical absorption is negligible over the wavelength range of interest. The low hysteresis in the cyclic voltammetry scan performed in 1N KOH, as seen in Figure 11b, indicates excellent chemical stability in this media. The chemical resistance is further evidenced in Figure 12 showing the surface of the optimized TiO<sub>2</sub> film (deposited onto nickel) after a three day immersion in KOH electrolyte.

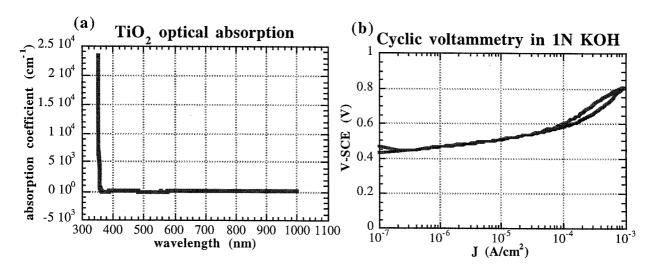


Figure 11: Optical absorption and KOH chemical stability in sputtered TiO<sub>2</sub> films.

Continued testing of the optical and protective properties of  $TiO_2$  is currently underway, as are characterizations of alternate materials such as a-SiC:H,  $MgF_2$  and  $CaF_2$ .



Figure 12: TiO<sub>2</sub> film surface after 3 day corrosion test in 1N KOH.

# Prototype photoreactor

To test the performance of the new integrated planar photoelectrode, we have designed and begun construction of a mid-sized prototype photoreactor. For containment of the KOH electrolyte, the reactor body is made of Teflon, with glass windows sealed on using gaskets and flanges, as shown in Figure 13. Up to six 1"x1" photoelectrodes can be installed and tested together. Reactor geometry effects the separation of hydrogen and oxygen gas generated at opposite sides of the photoelectrodes, and special ports are included for gas collection. The photoreactor is attached to a tripod with a standard swivel mount to facilitate solar tracking. The completed reactor will be able to accommodate installation of membranes between photoelectrodes for improved gas separation, and special feedthroughs to facilitate characterization of photoelectrode electronic and electrochemical performance.

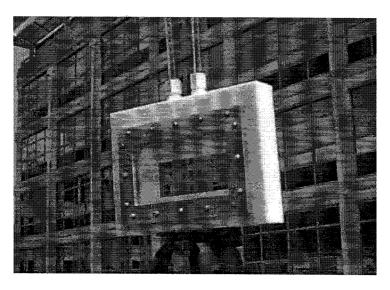


Figure 13: Prototype photoreactor for testing integrated planar photoelectrodes.

### **Summary and Plans**

In past years we have demonstrated direct solar-to-hydrogen conversion using photoelectrodes fabricated from low cost triple junction amorphous silicon solar cells with conversion efficiencies of 7.8%, representing 78% that of the solar cell's efficiency. Further improvement in the solar-to-hydrogen efficiency are can be expected with the use of higher efficiency MJ cells, and cells specifically optimized for hydrogen production. With proof of concept efficiency experiments completed, we have focussed this year on developing advanced photoelectrode designs, and on addressing the most critical materials issues vital to long term photoreactor stability. Substantial progress has been made in developing device quality amorphous silicon films with enhanced stability in KOH, transparent and conductive top-contact films of ITO with good KOH corrosion resistance, and highly transparent and protective TiO2 encapsulation films. We are currently continuing further optimization of the electrical and electrochemical properties of these and some alternative film materials. A new fully integrated thin-film photoelectrode was designed which will incorporate the best materials tested to date. Finalization of design details and fabrication of these photoelectrodes are in are near future plans. We are also finalizing the construction of a Teflon/glass photoreactor prototype for testing up to six photoelectrodes at a time. We will continue to explore new materials and different multilayer structures to take advantage of the best features of each for enhanced photoelectrode performance.

As an important example, the new photoelectrode design has opened the door to using side-by-side series-connected rather than only the stacked multijunction solar cells. As mentioned, this offers the possibility of using other low cost, thin film materials, such as coper-indium-diselenide cells which have reported solar efficiencies up to 18% (Tuttle et al., 1995).

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